1P098

Development of time-resolved absorption spectrometer to observe nano-sized particles fabricated by intense laser irradiation in supercritical fluid

（広大院・理[1]，広大自然セ[2]，JSTさきがけ[3]）○魏 紹禹[1]，加治屋 大介[2]，齋藤 健一[1, 2, 3]

【INTRODUCTION】 In a few years ago, we found a novel method for selective generation of nanomaterials by combining pulsed-laser ablation (PLA) method with supercritical fluid. This method allows us to obtain nanomaterials via a dry process by only changing the fluid density and/or temperature in ablation processes[1]. According to our recent results, nanomaterials, i.e. gold nanonecklace, huge gold nanosphere, light-emitting Si nanocrystal in visible region, were generated. Although such nanomaterials have been obtained, the generation mechanism has not been well understood yet. By elucidating reaction mechanisms of nano-sized particles, we can obtain further advanced materials and realize effective processes. To understand the reaction mechanisms after the laser irradiation to solid material immersed in the supercritical fluid, we developed a time-resolved absorption system, ranging from nanosecond to very long time scale of a few hundred hours *in situ* condition. By utilizing this system, we are able to discuss the generation mechanism of nano-sized particles fabricated by laser irradiation in the supercritical fluid.

【DEVELOPED INSTRUMENT】

An optical configuration of the developed system is schematically shown in Figure 1. The system consists of two parts: a nanosecond time-resolved absorption spectromator and a long-time absorption spectromator. The former part enables us to observe transient dynamics of generated nanoparticles, ranging from nanosecond to millisecond time region. This consists of a Q-switched double frequency (532nm) Nd:YAG laser as a pump beam, a xenon lamp as a probe beam, a polychromator equipped with an image intensified CCD (IICCD) camera, and optics. On the other hand, the latter one allows us to measure time-dependent spectra in a time scale from millisecond to hundreds hours. Such long time measurement is accomplished by using D_2 and halogen lamps, optical fibers, and another polychromator attached with a CCD camera, and allows us to observe nanocrystal growth process. Both parts are developed specially for *in situ* measurement of nanoparticle in supercritical fluid.

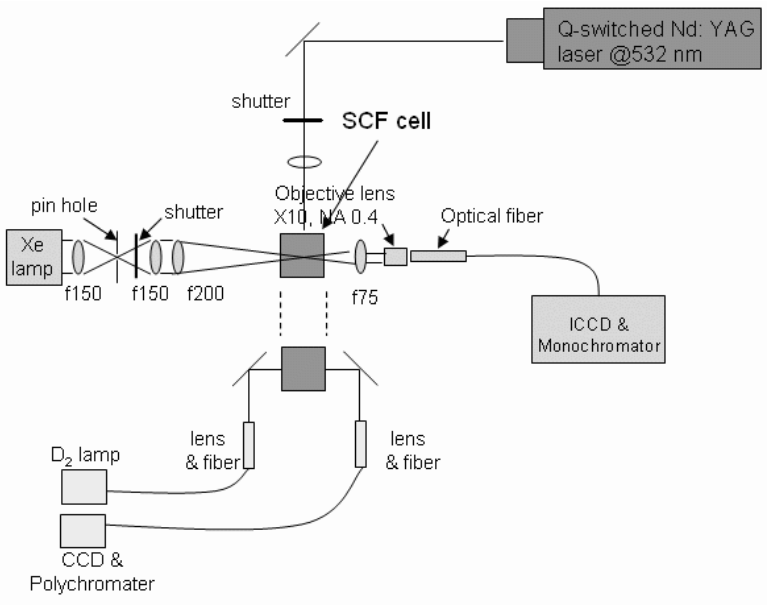

Fig.1. Schematic diagram of developed time-resolved absorption spectromator. This system consists principally of two spectromators, i.e. the nanosecond time-resolved absorption spectromator and the long-time absorption spectromator, ranging from millisecond to hundreds hours.

To observe nanoparticles generated by laser irradiation onto a gold plate immersed in supercritical fluid, an optical cell was constructed. As shown in Figure 2, the cell has four sapphire windows with a thickness of 5mm, which are sealed with O-rings made of nitrile rubber (NBR). We confirmed that the cell does not leak subtle CO_2 fluid at the pressure of 25 MPa during 24 hours. The cell is designed to have inlet and outlet ports to flow the fluid. That is, the sample fluid is refreshed in every laser shots by using a HPLC pump. The pressure is controlled by the HPLC pump and a valve and is measured with a strain gauge. The temperature is controlled by a set of cartridge heaters, a PID controller, and a thermocouple. Accordingly, we accomplished both pressure and temperature stabilities with a fluctuation of less than ±0.1% at 40℃ at 25 MPa.

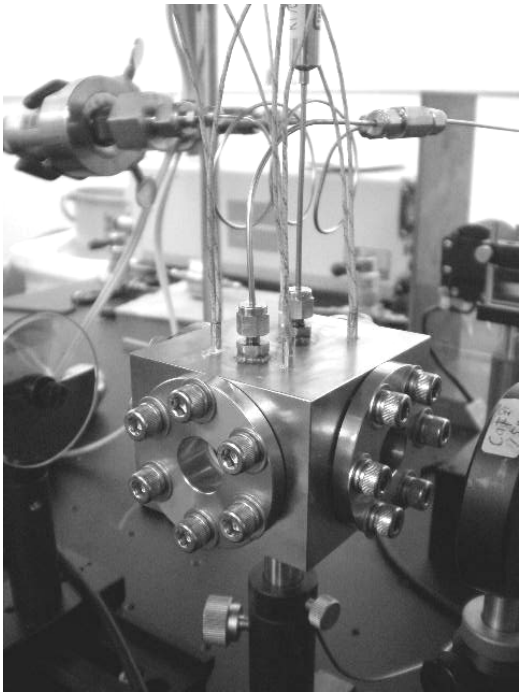

Fig.2. Developed optical cell to observe time-resolved absorption spectra of nanoparticles generated by laser irradiation in supercritical fluid

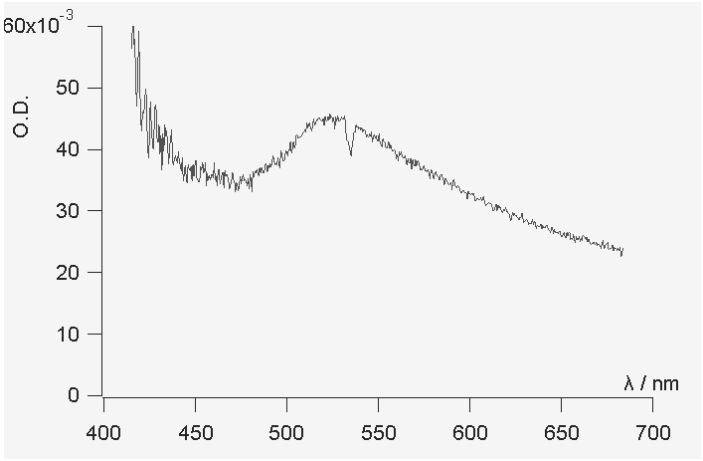

Fig.3. Absorption spectrum of gold nanoparticles at 70 ns after laser irradiation in supercritical CO_2

【RESULTS】

By using both two systems mentioned above, we realized the developed instrument to get absorbance of 10^{-3} (1 mOD) in a few minutes. Figure 3 shows a typical data of transient absorption spectra of generated gold nanoparticles in the supercritical CO_2. To the best of our knowledge, this is the first time to obtain the time-resolved absorption spectrum of nanoparticles, which are generated by the laser ablation of solid material in supercritical fluid. The nanoparticles in the present observation are generated by irradiating the laser of 25 mJ at 532 nm to the gold plate and probed at 70 ns later after the laser irradiation. Since the accumulation number and the repetition rate for collecting data are 20 times and 10 Hz, respectively, it takes a few minutes to obtain a single spectrum. As shown in Figure 3, the surface plasmon resonance band is clearly observed at around 520 nm.[2] This means that the generation of nanospheres starts within 70 ns after laser irradiation in the supercritical CO_2. By measuring the time profile of absorption at the single wavelength, we will be able to discuss both kinetics of gold nanoparticles immediately after laser irradiation and nanocrystal growing in the long-time region. These results will be mentioned in the conference.

[References]
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